DOI: 10.29302/Pangeea 23.28

EFFECTIVE WASHING AGENT FOR THE REMOVAL OF LEAD AND COPPER FROM MULTI-METAL CONTAMINATED SOILS IN MINING AREAS

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ABSTRACT: *Removal of heavy metals from soil by washing with different eco-friendly washing agents is one of the methods that has gained great interest in scientific research. As previous studies reported the potential of chitosan to be used as an eco-friendly washing agent for the removal of heavy metals from soils, in the present study, the removal of lead and copper from multi-metal contaminated soil collected from a mining area located in Zlatna (Alba County, Romania) by chitosan washing was investigated. Soil washing experiments were performed at laboratory scale by an ex-situ soil washing technique. A solid/liquid ratio (S/L ratio; g:mL) of 1:10, two concentrations of chitosan washing solution (2 and 5%) and different stirring times (120, 240, 360, 720, 1440 and 2400 min) were the studied parameters of the washing process. The results indicated that copper and lead removal efficiency increased with increasing the stirring time and the concentration of chitosan in the washing solution (in the case of Cu). In the investigated experimental conditions, about 55 % and 77% of copper and lead were removed from the soil after 2400 min of stirring with the chitosan washing solution.*

Keywords: *heavy metals; chitosan; soil washing; mining;*

Introduction

Soil pollution with heavy metals has long been recognized as a significant environmental problem observed both at the local, regional, national, and global levels due to the toxic influence of heavy metals on plants and animals and the risk of accumulation in agro-food products and it is possible to increase with the expansion of industrial activities, mining or areas contaminated with heavy metals [1]. Residues from mining and metallurgical operations contain various heavy metals (e.g. cadmium, copper, zinc, lead, arsenic, mercury) that are dispersed by wind and/or water after their disposal [2]. In soil, heavy metals are present in many chemical forms and generally possess different physical and chemical behaviors considering their chemical interactions, mobility, bioavailability and toxic potential. Furthermore, heavy metals are not degradable and can persist in soil for decades or even centuries [1].

Thus, because of this expansion and the long-term implications of heavy metals on the environment and human health, the application of appropriate technologies for the depollution of these soils is required to reduce the risk associated with heavy metal contamination.

In recent years, numerous soil remediation techniques based on physical, chemical and biological processes (e.g. immobilization, soil washing, encapsulation, phytoremediation, soil isolation and replacement, electrokinetic remediation, vitrification) have been used and investigated to address the increasing number of soils contaminated with heavy metals [3]. Several available technologies have been demonstrated through large-scale applications and are commercially available, while others are still being tested for application to heavy metal-contaminated sites [4]. Among these, immobilization, phytoremediation, and soil washing are frequently pointed out as the best demonstrated and available technologies (BAT) for the remediation of heavy metal-contaminated soils [5].

Soil washing is a physico-chemical decontamination method that uses water and various agents to extract pollutants adsorbed on fine soil particles. In the case of pollutants with poor solubility in aqueous solutions, such as heavy metals, the introduction of additives such as acids, bases, surfactants, solvents, chelating or separating agents into the washing process is necessary to achieve effective depollution [6].

However various studies have reported negative environmental effects related to conventional washing agents to remove heavy metals from contaminated soils [7,8]. Thus, in the last years, the attention of researchers has been directed towards the identification of natural substances, friendly to the environment, which could be as effective as synthetic washing agents.

Chitosan ((1-4)-2 amino-2-deoxy-A-D glucan) is a very abundant biopolymer derived from chitin (A-(1–4)-poly-N-acetyl-D-glucosamine), the second most abundant natural polysaccharide on earth after cellulose [9], and can be found in the exoskeleton of crustacea, insect's cuticles, algae and in the cell wall of fungi [10]. Currently, chitosan is receiving considerable attention because it is an excellent natural polymer for the removal of heavy metal ions due to the presence of the amine functional group (–NH2) and the amount of reactive hydroxyl functional groups (–OH), which act as chelating centers for metal ions, forming stable complexes [11].

Although many studies tested chitosan, under various forms, to remove heavy metals from wastewater [12-15], few studies attested the effectiveness of chitosan in extracting heavy metals from contaminated soil through washing [16] or amendments [17].

Therefore, this research aimed to evaluate the effectiveness of chitosan in removing lead and copper by washing multi-metal contaminated soil collected from a mining area located in Zlatna (Alba County, Romania). The influence of several parameters such as the concentration of washing solution and the stirring time was investigated for a solid/liquid ratio (S/L ratio; g:mL) of 1:10.

Materials and methods

2.1. Study area and soil sample

The mining activities in the Apuseni Mountains are well known due to the exploitations that have occurred for more than two millennia for non-ferrous and gold-silver ores. In Zlatna, there are numerous mining

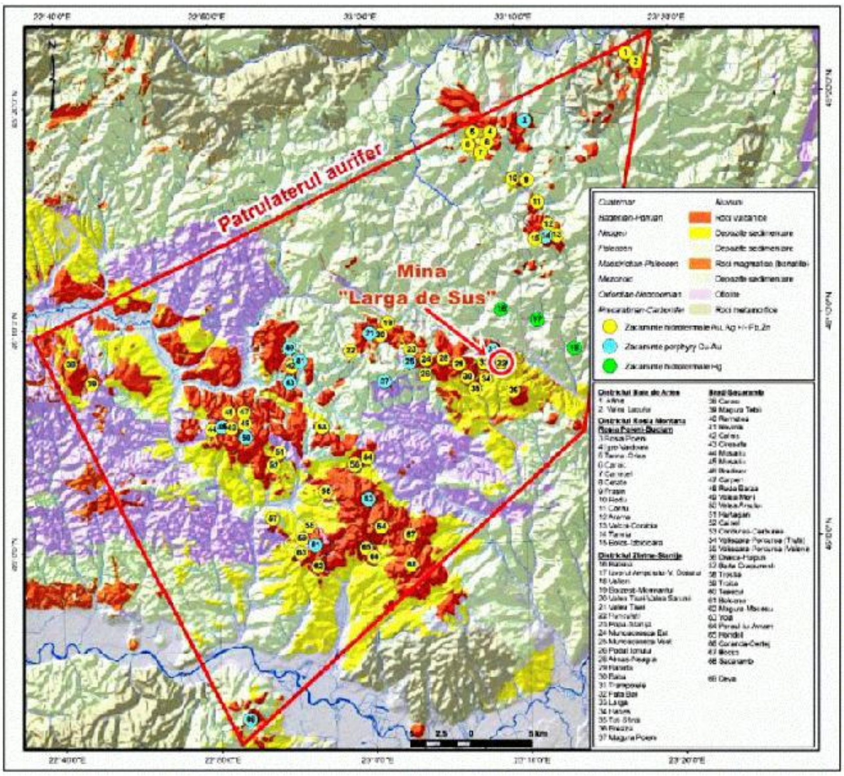

Fig. 1. Mineral deposits and occurrences within Transylvanian Gold Quadrangular (Apuseni Mountains) [20]

galleries and deposits of waste material dumped at the mouth of the mining galleries, which negatively impact the environment, in general, and the soil, in particular. Mining sites represent an important source of heavy metal contamination of soil, surface and groundwater, sediments and the atmosphere.

The studied mining perimeter "Larga de Sus" is located in Zlatna, Alba County and it falls within the Transylvanian Gold Quadrangular (Figure 1) which includes the Deva, Brad, Zlatna and Caraciu mining perimeters. The “Larga de Sus” mine is in the southeastern part of the Zlatna-St°nija volcanic alignment [18] and consists of an important pyrite body [19].

The mineralization related to the volcanic activity is of Au - Ag - Pb - Zn epithermal type and mineralogical paragenesis consists of pyrite, chalcopyrite, blende, galena, native gold, etc. [18, 21].

For soil washing experiments, an actual soil sample was collected from the “Larga de Sus” mining perimeter from about 700 m downstream of the “Larga de Sus” gallery.

The soil collected from the "Larga de Sus" mining perimeter was dried in the open air and used in washing experiments in a natural state. The soil sample was slightly acidic (pH 5.86) and classified as sandy soil. The concentration of heavy metals in the collected soil sample, determined through Atomic absorption spectrometry (AAS) was significant for Pb (633.05 mg kg>1) and Cu (424.81 mg kg>1). The investigated soil also contains various heavy metals such as Cr, Zn and Ni but in lower concentrations [22].

2.2. Chitosan sample and soil washing solution

The chitosan tested in the present research was obtained from shrimp exoskeletons and was provided by the Sigma-Aldrich company. In soil washing experiments chitosan was mixed with distilled water in the amount necessary to prepare a solution with a concentration of 2% and 5%.

To determine the concentration of heavy metals in chitosan washing solution, 33% hydrogen peroxide (H2O2) was added at a chitosan solution:H2O2 ratio of 1:3 (mL:mL) then the mixture was heated on a sand bath for 2 h, filtered and analysed for copper and lead content through AAS. The results obtained and the specifications of the chitosan provided by the Sigma-Aldrich company are indicated in Table 1.

Table 1. Characteristics of chitosan used

Parameter	Unit	Value	Parameter	Unit	Value
Loss on drying	%	6.2	Copper	mg l^{-1}	0.2
Sulfated ash	%	0.2	Lead	mg l^{-1}	<IDL*

2.3. Soil washing experiments and heavy metal analysis

Soil washing experiments were performed in a stirrer with continuous orbital rotation-oscillation, at room temperature, constant stirring speed (100 oscillations/min) and a solid/liquid ratio (S/L ratio; g:mL) of 1:10. Contaminated soil was put in contact with 2% and 5% chitosan washing solution for specific time intervals (120, 240, 360, 720, 1440 and 2400 min). Lead and copper concentration from soil was determined through AAS after a rigorous separation of soil from washing solution (filtration, repeated washing with distilled water, decanting and draining liquid). The average values of duplicate analyses were reported.

Before carrying out the AAS analysis, the depolluted soil samples using washing solution containing chitosan were dried in an oven at 95 C for about 1 hour. After that, a quantity of 3 g of the depolluted soil previously sieved through a 250 Wm mesh sieve was weighed on the electronic balance with a precision of 0.001 g.

After transferring this amount of depolluted soil into Berzelius glasses with a capacity of 100 mL, an amount of 1 mL of distilled water was added, which was introduced on the walls of the glass, then, under stirring, 21 mL of concentrated hydrochloric acid (HCl), followed by 7 mL of concentrated nitric acid (HNO3)

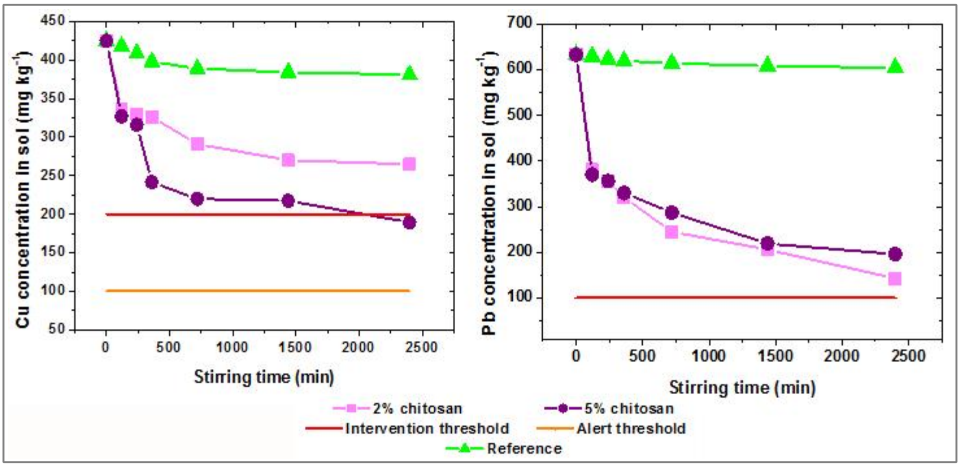

Fig. 2. The influence of washing solution concentration containing chitosan on Cu (a) and Pb (b) content in soil during the investigated stirring time

was added drop by drop to reduce foaming. The addition of acids was carried out under the exhaust niche.

After this step, the beakers were covered with glass and left for 3 hours for mineralization (disaggregation) on the sand bath, under the niche, until the decontaminated soil samples became slightly gelatinous.

After mineralization and cooling of the samples, they were passed in a 100 mL volumetric flask through filter paper that was washed twice with distilled water. After filtration, the supernatants were brought to the mark in 100 mL volumetric flasks, transferred into plastic containers and stored in a refrigerator until the determination of heavy metal content.

Heavy metal removal efficiency was quantitatively determined using the following equation [23]:

$$Removal\ efficiency\ (\%)=(C_0-C_f)/C_0\ ]100$$

where C_0 is the initial metal concentration in the soil sample (mg kg-1) and C_f is the final concentration of metals in the soil (mg kg-1), after the soil washing treatment.

The results obtained after soil washing experiments were compared with a reference, in which the soil was washed only with distilled water.

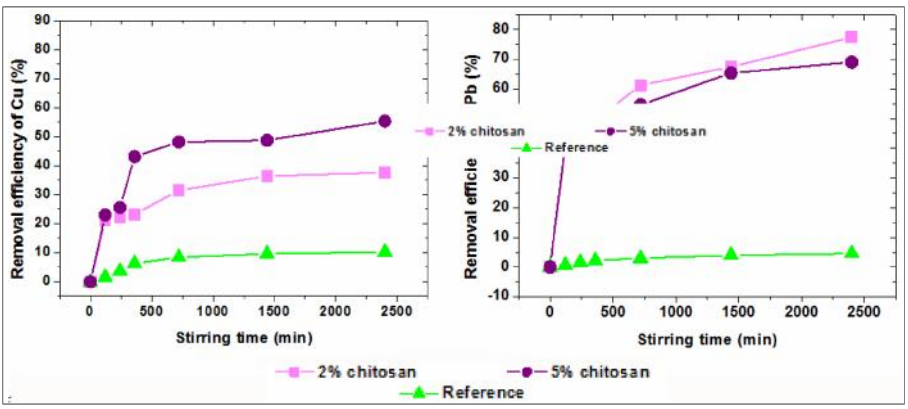

Fig. 3. Removal efficiency of Cu (a) and Pb (b) from soil during the investigated stirring time

3. Results and discussion

The variation of lead and copper concentration in the soil during the washing with chitosan is indicated in Figure 2 (a, b) while the values of the removal efficiency are illustrated in Figure 3 (a, b).

As expected, increasing the concentration of the washing solution containing chitosan from 2% to 5% leads to a better mobilization of copper from the soil and thus to a more pronounced decrease in the concentration of Cu from the soil during the investigated stirring time.

Thus, increasing the concentration of the washing solution containing chitosan to 5% results in a decrease of Cu concentration in the soil below the intervention threshold (200 mg kg-1) according to Romanian legislation [24] by 10.58 mg kg-1 after 2400 minutes.

The increase in copper mobilization from the soil with increasing the concentration of chitosan washing solution may be due to the introduction of more active sites available for metal ion binding [25]. Similar results were obtained by Jiang et al. (2011) when studied the influence of chitosan concentration in washing solution for copper and nickel extraction from soil [16]. The removal of copper and nickel from soil increased with increasing chitosan concentration from 0.10 gL-1 to 0.40 gL-1 [16].

Increasing the concentration of the washing solution containing chitosan from 2% to 5% does not lead to a decrease in the soil Pb content during the investigated stirring time, except for the value recorded after 120 minutes of stirring, when by increasing the concentration of the washing solution containing chitosan from 2% to 5%, the soil Pb concentration decreased slightly from 380 mg kg-1 to 370 mg kg-1. In the rest of the investigated stirring time, the concentration of Pb in the soil had a lower level in the case of using the washing solution containing chitosan in a concentration of 2% (143,00-320,00 mg kg-1) than when the washing solution contained 5% chitosan (196,00-330,00 mg kg-1).

As can be seen from Figure 2b, although the concentration of lead in the soil under the investigated experimental conditions decreased by more than 4.4 times compared to the initial value, the intervention threshold of 100 mg kg-1, provided by the Romanian legislation in the case of lead [24] was not achieved.

However, the presence of chitosan in the washing solution leads to a better mobilization of copper and lead from the soil than when the washing solution does not contain chitosan (reference samples), as indicated in Figure 2.

Increasing the concentration of the washing solution containing chitosan from 2% to 5% results in an increase of Cu removal efficiency with values between 1.96% and 19.88%, during the investigated stirring time. Also, the removal efficiency of copper from soil increases by up to 6.8 times when chitosan is present in the washing solution.

In the case of Pb, when the concentration of chitosan washing solution was increased from 2% to 5%, the removal efficiency slightly decreased from values between 49.4% and 77.4% to 47.8% and 69%. Thus, the highest Pb removal efficiency (77.4%) was observed when washing solution contained 2% chitosan, while only 69% Pb was removed when using washing solution containing 5% chitosan. As it was also identified by other researchers [25] this fact may be due to the remaining of active centers from the excess chitosan introduced in the washing process in a free state or the formation of complexes with the active metal binding centers from the structure of chitosan by other elements or metals present in the soil sample (Fe, Ca, Al, Cu, Zn, Cr, Ni).

As regards the influence of the stirring time on the removal efficiency of copper and lead from soil using washing solution containing chitosan, the removal of investigated heavy metals occurs relatively quickly and increases with increasing the stirring time. Thus, the removal efficiency of Cu reaches 43.1% after 360 minutes of stirring when using washing solution with 5% chitosan.

After this stirring time (360 minutes), the copper removal efficiency increased slightly during the rest of the investigated stirring time showing a slight plateau. Thus, 48.2%, 48.7%, and 55.4% Cu was removed after 720, 1440, and 2400 minutes of stirring, respectively (washing solution with 5% chitosan). The same fact was observed when the washing solution contained 2% chitosan. Therefore, 21%, 22.3%, 23.2%, 31.4%, 36.4% and 37.6% Cu was removed after 120, 240, 360, 720, 1440, and 2400 minutes of stirring, respectively.

Regarding the removal of lead from the investigated soil, 41.5% Pb was removed after 120 minutes of stirring (washing solution with 5% chitosan). During the rest of the investigated stirring time, Pb removal efficiency increased gradually, for both concentrations of washing solution. At the end of the investigated stirring time, more than 77% of Pb was removed from the studied soil (washing solution with 2% chitosan).

In the investigated experimental conditions, 77.4% Pb and 55.4% Cu were removed from the soil collected from the "Larga de Sus" mining perimeter after 2400 minutes of stirring.

It should be pointed out that a solid:liquid ratio of 1:10 (g:mL) was sufficient to reduce the Cu concentration from studied soil below the intervention threshold established by Romanian legislation, after 2400 min of stirring. Instead, in the case of Pb, the values established by legislation were not reached, but the lead concentration from soil decreased more than 4 times compared to the initial value.

The results obtained during the soil washing experiments indicate that chitosan may be successfully used as a washing agent and has good potential to remove Cu and Pb from the multi-metal polluted soil from the "Larga de Sus" mining perimeter.

4. Conclusions

In the present study, chitosan has been proven an effective soil-washing agent for the removal of Cu and Pb from the multi-metal polluted soil from the "Larga de Sus" mining perimeter.

In the investigated experimental conditions, the removal of Cu and Pb from studied soil occurs relatively quickly, the removal efficiency of Cu reached 43.1% after 360 minutes of stirring, while the removal efficiency of Pb reached 41.5% after 120 minutes of stirring when the washing solution with 5% chitosan was used. A solid:liquid ratio of 1:10 (g:mL) was sufficient to reduce the Cu concentration from the studied soil below the intervention threshold established by Romanian legislation, after 2400 min of stirring and the lead concentration from the soil decreased more than 4 times compared to the initial value. The best removal efficiencies were obtained after 2400 minutes of stirring of contaminated soil with chitosan solution when 77.4% Pb and 55.4% Cu were removed from the investigated multi-metal contaminated soil.

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